

Title	Photoactivated N-Acyliminoiodinanes Applied to Amination: an ortho-Methoxymethyl Group Stabilizes Reactive Precursors
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Ortho-effect-enabled characterization of *N*-acyliminoiodinane and its application to photo-induced amination

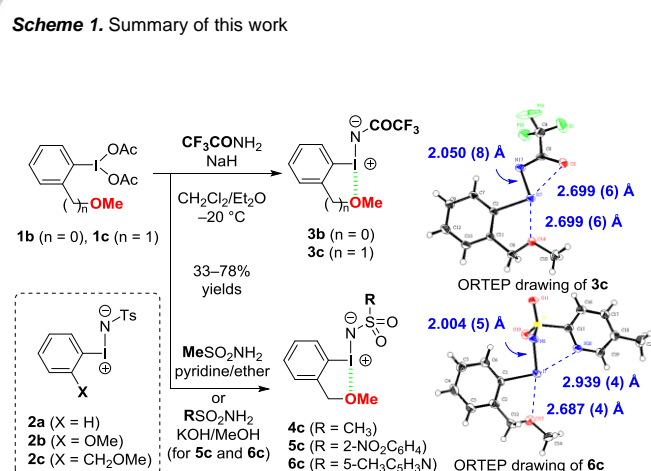
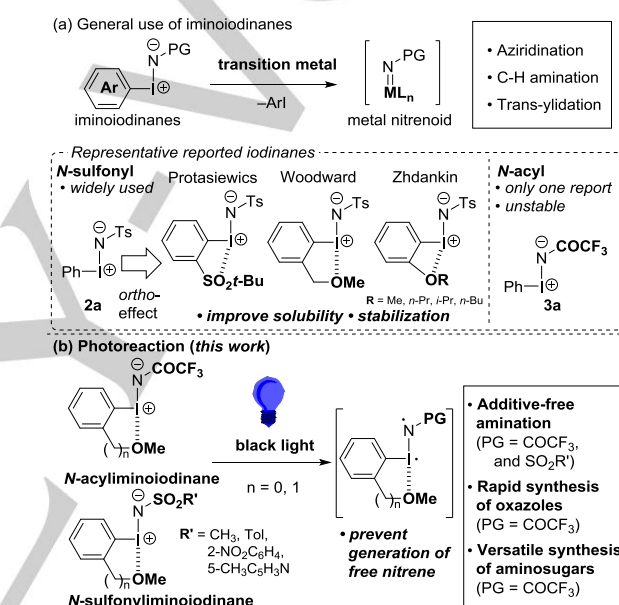
Yusuke Kobayashi,^[a] Sota Masakado,^[a] Yoshiji Takemoto^{*[a]}

Abstract: *N*-acyliminoiodinanes have been characterized for the first time by X-ray structural analysis. The *ortho*-methoxymethyl group and the carbonyl oxygen coordinate to the iodine atom of the iminoiodinane. The activation of the *N*-acyliminoiodinane was achieved by photo-irradiation at 370 nm to enable reaction with various silyl enol ethers to give α -aminoketone derivatives in good to high yield. It was also demonstrated that *N*-sulfonyliminoiodinanes bearing *ortho*-substituents could be used in the photo-induced amination.

Iminoiodinanes^[1,2] have been established as a useful source of nitrogen, and a variety of these molecules, including natural products, have been synthesized or functionalized via transition-metal-catalyzed aziridination, C–H amination, and trans-ylidation (Scheme 1a).^[3,4] Due to their poor solubility in organic solvents, derivatization to more a soluble form by introducing an *ortho*-coordinating substituent has been developed to date.^[5] As representative examples, iminoiodinanes bearing *ortho*-sulfonyl,^[6] alkoxy,^[7] and methoxymethyl^[8] substituents, developed by Protasiewicz, Zhndankin, and Woodward, respectively (Scheme 1a), improved the solubility, and those structures were successfully characterized by X-ray analyses. Most of the reported *N*-protecting groups are, however, limited to *N*-sulfonyl groups, such as tosyl and nosyl groups, and only one report has been made on the synthesis and reactivity of an *N*-acyliminoiodinane, presumably due to their lability toward Hofmann rearrangement and/or hydrolysis.^[9] In fact, although *N*-trifluoroacetylminoiodinane **3a** has been synthesized and reacted with an alkene under iron-catalysis, **3a** was reported to be unstable,^[10] and the corresponding aziridine was only obtained in ca. 50% yield. However, direct introduction of an *N*-trifluoroacetamido group is a useful transformation, as the *N*-trifluoroacetamido group offers several salient features; 1) improved biological activities,^[11] 2) relatively easy manipulation and deprotection toward the synthesis of complex molecules,^[12] Alternative activation approaches, such as Lewis acid catalysis,^[7] Brønsted acid catalysis,^[13] molecular iodine catalysis,^[14] and thermal activation,^[15] have been recently developed, particularly to avoid heavy-metal contamination of active pharmaceutical ingredients.^[16] We envisioned that *ortho*-substituents would stabilize the *N*-trifluoroacetylminoiodinane, as well as improve its solubility, to enable its isolation (Scheme 1b). Furthermore, such coordinating groups would also stabilize the photo-excited state of the iminoiodinane, preventing generation of free nitrenes,^[17] which can afford undesired products through non-selective reactions. Instead, the desired amidyl radical species^[14,18] would be generated to achieve additive-free amination.

We first tried to prepare several *N*-trifluoroacetylminoiodinanes bearing *ortho*-substituents (**3**) from trifluoroacetamide and the corresponding iodobenzene diacetate **1b,c**^[7,8] under basic conditions (Scheme 2). Among the bases investigated, sodium hydride was most suitable for the synthesis of **3** in terms of basicity and anhydrous condition. *ortho*-Methoxymethyl variant **3b** was difficult to

isolate, mostly due to its instability during purification, however, iminoiodinane **3c** with an *ortho*-methoxymethyl substituent was successfully prepared^[19,20] and was isolated as a pale yellow crystalline solid which could be stored for several months in the freezer. Several new *N*-sulfonyliminoiodinanes **4c**, **5c**, and **6c** with *ortho*-methoxymethyl substituents were prepared under the conventional conditions,^[1] along with the known iminoiodinanes **2a–2c**.



As expected, the ORTEP drawings of the X-ray structures of **3c** and **6c** indicated that the oxygen atom of the *ortho*-methoxymethyl group coordinates to the iodine atom in all cases (I–O distance was 2.687–2.699 Å, Scheme 2). Interestingly, the distance between the iodine atom of **3c** and the carbonyl oxygen atom of the *N*-trifluoroacetyl

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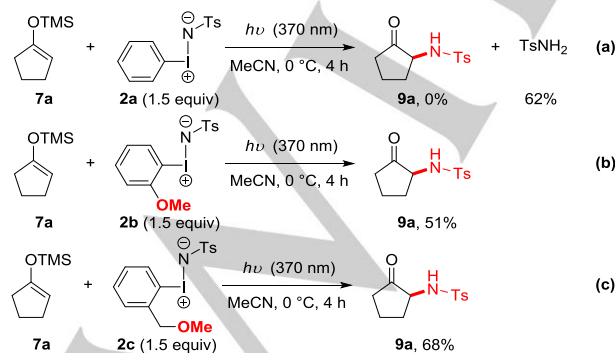
group was also within the sum of the Van der Waals radii, and **3c** was obtained as a monomeric structure with no obvious intermolecular interactions, contrary to the previously reported X-ray structures of *N*-sulfonyliminoiodinanes.^[6–8] The N–I bond length was 2.050 Å, which is almost identical to that of *N*-iodosuccinimide (2.059 Å),^[21] and slightly longer than those of *N*-sulfonyliminoiodinanes (1.990–2.039 Å).^[6–8] Based on the X-ray structure of **3c**, natural population analysis was performed at the MP2/6-311+G(d,p) level^[22] using Gaussian 09.^[23] The calculated charges of iodine, nitrogen, and the carbonyl oxygen were +1.15, –0.81, and –0.80, respectively. These results indicate that the I–N bond is a highly polarized single bond,^[6,24] and the negative charge is delocalized between amide nitrogen and the oxygen atoms. The isolated solid **6c** was also obtained as a monomer, presumably due to the dual coordination of the *ortho*-methoxymethyl group and the pyridyl group.^[19]

Table 1: Optimization of photo-induced α -amination of **7a** with **3c**

Entry	h ν	solvent	8a (%) ^[a]
1	Xenon lamp (235–1050 nm)	CH ₃ CN	39 ^[b]
2	Xenon lamp (254 nm) ^[c]	CH ₃ CN	0
3	Xenon lamp (300 nm) ^[c]	CH ₃ CN	35
4	Xenon lamp (350 nm) ^[c]	CH ₃ CN	51
5	Xenon lamp (370 nm) ^[c]	CH ₃ CN	77 (68 ^[b])
6	Xenon lamp (400 nm) ^[c]	CH ₃ CN	49
7	Xenon lamp (440 nm) ^[c]	CH ₃ CN	0
8	Xenon lamp (370 nm) ^[c]	CH ₂ Cl ₂	47
9	Xenon lamp (370 nm) ^[c]	Et ₂ O	49
10	Xenon lamp (370 nm) ^[c]	CH ₃ NO ₂	32

[a] Unless otherwise noted, ¹H NMR yields based on 4-nitroanisole as an internal standard. [b] Isolated yields. [c] Band-pass filters (half width ca. 10 nm) were used.

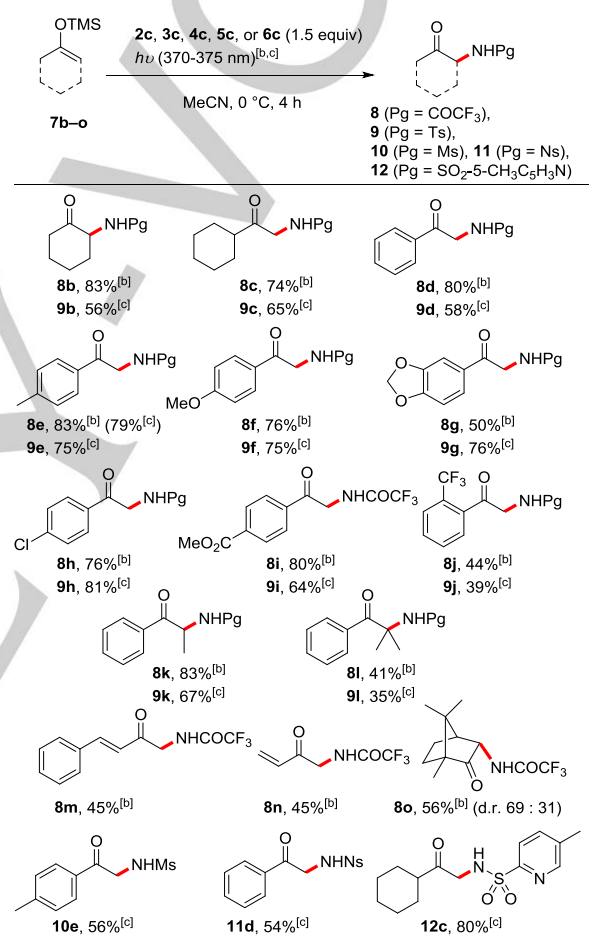
We then investigated the reaction of **3c**, and α -amination of silyl enol ether **7a** was chosen as the model reaction^[25,26] (Table 1). To our surprise, the reactivity toward transition metal^[1] and Lewis acid^[7,27] was totally different to that of the *N*-sulfonyliminoiodinanes, and no desired product **8a** was obtained.^[19] To our delight, the desired product **8a** was obtained under photo-irradiation conditions (xenon lamp, 235–1050 nm), albeit in 39% yield (entry 1). Encouraged by this result, we next investigated different wavelengths using band-pass filters (entries 2–7). Among the wavelengths tested, 370 nm was found to be the most suitable for the promotion of the reaction to furnish **8a** in 77% yield (entry 5). Under irradiation with the optimized wavelength (370 nm), different solvents were then investigated (entries 8–10), and MeCN gave the best result in terms of chemical yield.



Scheme 3: Effect of *ortho*-substituents

To examine the generality and effect of the substituent, we next investigated α -amination of silyl enol ether **7a** with *N*-tosyliminoiodinanes **2a–c** bearing different *ortho*-substituents (Scheme 3). Under photo-irradiation conditions, iodine **2a** with no substituent afforded none of the desired product **9a**. Only decomposed *N*-tosylamide was obtained in 62% yield, probably due to the insolubility of **2a** in acetonitrile (Scheme 3a). In contrast, iminoiodinanes **2b** and **2c** were fairly soluble in acetonitrile, and afforded the α -aminated product **9a** in 51% and 68% yields, respectively, by simple photo-irradiation (Scheme 3b, and 3c). The decomposition rate of **2c** by TLC monitoring was slower than that of **2a** and **2b**,^[20] which translates to a higher chemical yield of **9a** with **2c**.

Table 2: Substrate scope of black light-induced α -amination of **7** with iminoiodinanes^[a]



[a] Isolated yields. [b] A 300 W xenon lamp fitted with a band-pass filter (half width ca. 10 nm) was used. [c] LED light (peak wavelength 375 \pm 3 nm) was used.

Having identified the optimized reaction conditions and applied these to *N*-sulfonyliminoiodinanes, we next investigated substrate scope of both the silyl enol ether and the iminoiodinanes (Table 2). Various cyclic and acyclic silyl enol ethers were amenable to the present photo-induced reaction with **3c** to give the corresponding adducts **8b–j** in 44–83% yields. Notably, readily available LED light was found to be sufficient to promote the reaction to obtain **8e** without a significant decrease in yield (Xenon lamp: 83%, LED light: 79%). α -Mono- and α,α -di-substituted silyl enol ethers also afforded the secondary and tertiary aminoketones **8k** and **8l** in 83% and 41% yields, respectively. Similarly, introduction of *N*-tosylamido groups at the α -position of a variety of silyl enol ethers gave a smooth reaction

with **2c** under simple irradiation by LED light to obtain **9b–l** in 35–76% yields. A unique reactivity of **3c** was observed when electron-rich enol moieties could be reacted in preference to other alkene moieties to afford **8m** and **8n**, whereas **2c** gave complex mixtures. Furthermore, the photo-induced reactions of novel *N*-sulfonyliminoiodinanes **4c**, **5c**, and **6c** produced *N*-mesyl, *N*-nosyl, and *N*-pyridinesulfonyl α -aminoketones in 54–80% yields, demonstrating the generality of this methodology. Iodine **6c**, with a dual coordinating group, exhibited superior stability, even when stored at room temperature.

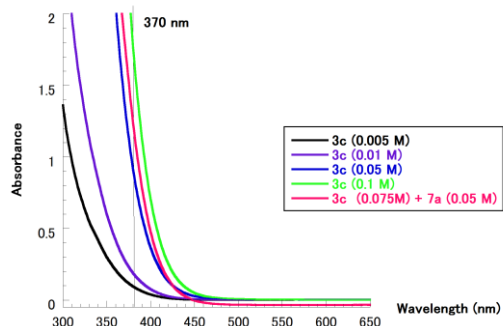
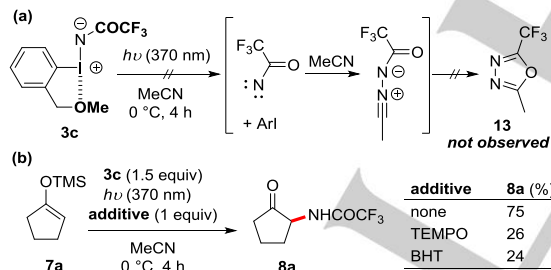


Figure 1: UV-VIS absorption of **3c** in acetonitrile

UV-VIS spectrum of **3c** was measured in acetonitrile (Figure 1). Although the maximum absorption peak was at 229 nm, corresponding to aromatic ring, we did observe an absorbance at approximately 370 nm, even at a lower concentration than the standard reaction conditions (0.075 M) and in the presence of silyl enol ether **7a**. To gain deeper insight into the photo-activation, we next calculated the excitation energy of **3c** using a DFT-TD^[28] method, based on the optimized X-ray structure. As a result, three excitation wavelengths were found (364, 304, and 275 nm). The energy gap between the HOMO and LUMO corresponded to the 365 nm wavelength (Figure S1),^[19] which is likely to trigger the reaction with silyl enol ether.

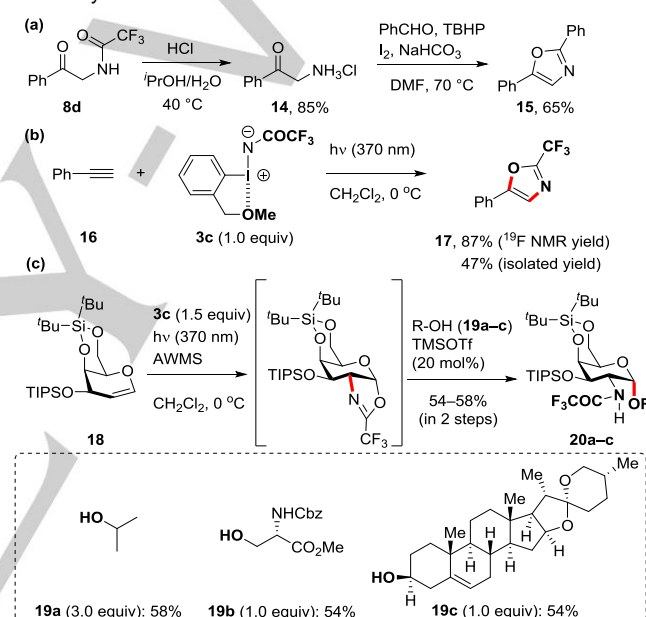


Scheme 4: (a) Exclusion of an acylnitrene as an intermediate (b) Effect of radical scavengers.

We then conducted several control experiments to try to understand the reaction mechanism (Scheme 4a, b). Generation of an *N*-acylnitrene species^[17] could not be involved under the present reaction conditions, as it has been reported that such species immediately insert into acetonitrile to afford oxadiazole **13**, whose characteristic ¹⁹F NMR peak at –66.8 ppm was not observed at all (Scheme 4a). The addition of a radical scavenger, such as TEMPO or BHT, significantly decreased the chemical yield of **8a** when silyl enol ether **7a** and iodane **3c** reacted under photo-irradiation conditions, suggesting that a radical intermediate is involved in the reaction (Scheme 4b). Although further mechanistic studies are required, it was postulated that the silyl enol ether would attack the photo-excited σ^* (N–I) orbital (Figure S3) of the *N*-acyliminoiodinane

3c, similar to the reaction mechanism of sulfonylbromane, suggested by Ochiai, Miyamoto, and Nakanishi et al.^[9,24b,c]

Finally, further applications of this method were demonstrated (Scheme 5). The trifluoroacetyl group of **8** can be easily deprotected under mildly acidic conditions, providing α -aminoketone hydrochloride **14**, a key intermediate for various heterocycles,^[12a,b] in high yield. Oxazole **15** was synthesized from **14** by simple oxidative coupling with an aldehyde (Scheme 5a). Notably, photo-induced reaction of **3c** with phenylacetylene **16** afforded trifluoromethylated oxazole **17** (Scheme 5b), and this transformation is inaccessible by the previously reported iminoiodinanes. In addition, a concise and versatile synthesis of aminosugars^[29] was achieved using this photo-induced reaction (Scheme 5c). Thus, treatment of glycal **18** with **3c** under photo-irradiation gave an oxazolidine intermediate,^[29,30a] which underwent Lewis-acid-catalyzed glycosylation with a series of alcohols **19a–c** to afford the corresponding aminosugar-conjugates **20a–c** in 54–58% yields.^[31] This type of 1,2-aminoalcoxylation is sometimes difficult using *N*-sulfonyliminoiodinanes due to the relative instability of the aziridine intermediate,^[29,30b,32] whereas conjugation with aminosugars offers a powerful tool for drug discovery.^[11,33]



Scheme 5: (a) Deprotection and derivatization of product **8** (b) Application to trifluoromethylated oxazole synthesis (c) Application to aminosugar synthesis

In conclusion, we have demonstrated that the coordination of an *ortho*-methoxymethyl group effectively stabilizes *N*-acyliminoiodinanes, enabling the first synthesis and characterization of their structure. The X-ray structure revealed that the carbonyl oxygen atom coordinates to the iodine atom of the iminoiodinane. In addition, the *N*-acyliminoiodinane could be activated to react with silyl enol ethers under photo-irradiation conditions. This methodology was successfully expanded to various *N*-sulfonyliminoiodinanes. We believe that the present activation method of iodinanes will encourage greener approaches for the introduction of amino groups and further develop the understanding of hypervalent iodine chemistry.^[34] Further investigation of the detailed reaction mechanism and more diverse applications are now underway in our laboratory.

Experimental Section

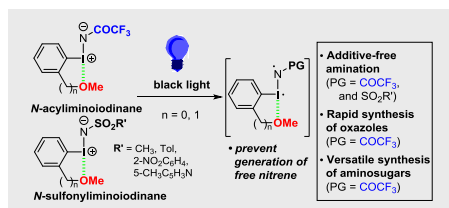
Silyl enol ether **7a** (0.10 mmol, 15.6 mg) and iminoiodinane **3c** (0.15 mmol, 53.9 mg) were dissolved in MeCN (2.0 mL), and the reaction mixture was stirred at 0 °C for 4 h under photo-irradiation by LED light (peak wavelength 375 ± 3 nm). After concentration under reduced pressure, the reaction mixture was directly purified by silica gel column chromatography (Hexane : EtOAc = 80 : 20) to give **8a** (14.7 mg, 71%).

Acknowledgements

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- [1] For recent reviews on iminoiodinanes, see: (a) P. Dauban, R. H. Dodd, *Synlett* **2003**, 11, 1571. (b) J. W. W. Chang, T. M. U. Ton, P. W. H. Chan, *Chem. Rev.* **2011**, 11, 331. (c) J. L. Roizen, M. E. Harvey, J. Du Bois, *Acc. Chem. Res.* **2012**, 45, 911. (d) B. Darses, R. Rodrigues, L. Neuville, M. Mazurais, P. Dauban, *Chem. Commun.* **2017**, 53, 493. (e) J. M. Alderson, J. R. Corbin, J. M. Schomaker, *Acc. Chem. Res.* **2017**, 50, 2147.
- [2] For selected reviews on hypervalent iodine chemistry, see: (a) V. V. Zhdankin, P. J. Stang, *Chem. Rev.* **2008**, 108, 5299. (b) M. Ochiai, *Synlett* **2009**, 159. (c) T. Dohi, Y. Kita, *Chem. Commun.* **2009**, 2073. (d) V. V. Zhdankin, *Hypervalent Iodine Chemistry: Preparation, Structure, and Synthetic Applications of Polyvalent Iodine Compounds*, Wiley, New York, 2013. (e) F. V. Singh, T. Wirth, *Chem. Asian J.* **2014**, 9, 950. (f) R. Narayan, S. Manna, A. P. Antonchick, *Synlett* **2015**, 26, 1785. (g) A. Yoshimura, V. V. Zhdankin, *Chem. Rev.* **2016**, 116, 3328.
- [3] For selected recent reviews on C–H amination, see: (a) J. Jiao, K. Murakami, K. Itami *ACS Catal.* **2016**, 6, 610. (b) Y. Park, Y. Kim, S. Chang, *Chem. Rev.* **2017**, 117, 9247.
- [4] For selected recent examples using iminoiodinanes, see: (a) J. Li, J. S. Cisar, C.-Y. Zhou, B. Vera, H. Williams, A. D. Rodríguez, B. F. Cravatt, D. Romo, *Nat. Chem.* **2013**, 5, 510. (b) K. Tokumasu, R. Yazaki, T. Ohshima, *J. Am. Chem. Soc.* **2016**, 138, 2664. (c) A. Saito, *ARKIVOC* **2017**, 84. (d) L. Maestre, R. Dorel, Ó. Pablo, I. Escofet, W. M. C. Sameera, E. Álvarez, F. Maseras, M. Mar Díaz-Requejo, A. M. Echavarren, P. J. Pérez, *J. Am. Chem. Soc.* **2017**, 139, 2216.
- [5] For a review on *ortho*-coordinating groups, see: V. V. Zhdankin, J. D. Protasiewicz, *Coord. Chem. Rev.* **2014**, 75, 54.
- [6] (a) M. Boucher, D. Macikenas, T. Ren, J. D. Protasiewicz, *J. Am. Chem. Soc.* **1997**, 119, 9366. (b) D. Macikenas, E. Skrzypczak-Jankun, J. D. Protasiewicz, *J. Am. Chem. Soc.* **1999**, 121, 7164. (c) B. V. Mephrath, J. D. Protasiewicz, *ARKIVOC* **2003**, 83.
- [7] A. Yoshimura, V. N. Nemykin, V. V. Zhdankin *Chem. Eur. J.* **2011**, 17, 10538.
- [8] (a) A. J. Blake, A. Novak, M. Davies, R. I. Robinson, S. Woodward, *Synth. Commun.* **2009**, 39, 1065.
- [9] M. Ochiai, K. Miyamoto, S. Hayashi, W. Nakanishi, *Chem. Commun.* **2010**, 46, 511.
- [10] D. Mansuy, J.-P. Mahy, A. Dureault, G. Bedi, P. Battioni, *J. Chem. Soc. Chem. Commun.* **1984**, 1161.
- [11] A. Sandomenico, A. Russo, G. Palmieri, P. Bergamo, M. Gogliettino, L. Falcigno, M. Ruvo, *J. Med. Chem.* **2012**, 55, 2102. (b) S. K. Mamidyal, S. Dutta, B. A. Chrunyk, C. Prévile, H. Wang, J. M. Withka, A. McColl, T. A. Subashi, S. J. Hawrylik, M. C. Griffor, S. Kim, J. A. Pfeifferkorn, D. A. Price, E. Menhaji-Klotz, V. Mascitti, M.G. Finn, *J. Am. Chem. Soc.* **2012**, 134, 1978.
- [12] For a review, see: (a) S. E. Lopez, J. Restrepo, J. Salazar, *Cur. Org. Synth.* **2010**, 7, 414. For selected examples, see: (b) M. Osorio-Olivares, M. C. Rezende, S. Sepulveda-Boza, B. K. Cassels, A. Fierro, *Bioorg. Med. Chem.* **2004**, 12, 4055. (c) K. Kong, Z. Moussa, C. Lee, D. Romo, *J. Am. Chem. Soc.* **2011**, 133, 19844.
- [13] (a) A. A. Lamar, K. M. Nicholas, *J. Org. Chem.* **2010**, 75, 7644. (b) K. Kiyokawa, T. Kosaka, S. Minakata, *Org. Lett.* **2013**, 15, 4858. (c) A. C. Brueckner, E. N. Hancock, E. J. Anders, M. M. Tierney, H. R. Morgan, K. A. Scott, A. A. Lamar, *Org. Biomol. Chem.* **2016**, 14, 4387.
- [14] B.-W. Lim, K.-H. Ahn, *Synth. Commun.* **1996**, 26, 3407.
- [15] C. Tejo, H. Q. Yeo, P. W. H. Chan, *Synlett* **2014**, 25, 201.
- [16] J. Magano, J. Dunetz, *Chem. Rev.* **2011**, 111, 2177.
- [17] (a) V. Desikan, Y. Liu, J. P. Toscano, W. S. Jenks, *J. Org. Chem.* **2008**, 73, 4398. (b) M. P. Sherman, W. S. Jenks, *J. Org. Chem.* **2014**, 79, 8977.
- [18] For selected recent examples, see: (a) K. Matsuzawa, Y. Nagasawa, E. Yamaguchi, N. Tada, A. Itoh, *Synthesis* **2016**, 48, 2845. (b) J. Davies, T. D. Svestrup, D. F. Reina, N. S. Sheikh, D. Leonori, *J. Am. Chem. Soc.* **2016**, 138, 8092. (c) M. D. Kärkä, *ACS Catal.* **2017**, 7, 4999. (d) C. B. Tripathi, T. Ohtani, M. T. Corbett, T. Ooi, *Chem. Sci.* **2017**, 8, 5622.
- [19] See the Supporting Information for details.
- [20] It was reported that an *ortho*-alkoxymethyl group stabilized the iodonium(III) ylide better than an *ortho*-alkoxy group, see: L. Wang, O. Jacobson, D. Avdic, B. H. Rotstein, I. D. Weiss, L. Collier, X. Chen, N. Vasdev, S. H. Liang, *Angew. Chem. Int. Ed.* **2015**, 54, 12777.
- [21] K. Pandmanabhan, I. C. Paul, D. Y. Curtin, *Acta Cryst.* **1990**, C46, 88.
- [22] (a) C. Möller, M. S. Plesset, *Phys. Rev.* **1934**, 46, 618; (b) J. Gauss, *J. Chem. Phys.* **1993**, 99, 3629; (c) J. Gauss, *Ber. Bunsen-Ges. Phys. Chem.* **1995**, 99, 1001.
- [23] Gaussian 09, Revision C.01, M. J. Frisch, *et al.* Gaussian, Inc., Wallingford CT, 2009.
- [24] (a) A. K. Mishra, M. M. Olmstead, J. J. Ellison, P. P. Power, *Inorg. Chem.* **1995**, 34, 3210. For related hypervalent *N*-sulfonyliminobromanes, see: (b) M. Ochiai, T. Kaneaki, N. Tada, K. Miyamoto, H. Chuman, M. Shiro, S. Hayashi, W. Nakanishi, *J. Am. Chem. Soc.* **2007**, 129, 12938. (c) M. Ochiai, K. Miyamoto, T. Kaneaki, S. Hayashi, W. Nakanishi, *Science* **2011**, 332, 448.
- [25] D. A. Evans, M. M. Fad, M. T. Bilodeau, *J. Am. Chem. Soc.* **1994**, 116, 2742.
- [26] J. Du Bois, J. Hong, E. M. Carreira, M. W. Day, *J. Am. Chem. Soc.* **1996**, 118, 915.
- [27] For an organo-Lewis-acid-catalyzed activation of hypervalent iodine reagents, see: M. Saito, Y. Kobayashi, S. Tsuzuki, Y. Takemoto, *Angew. Chem. Int. Ed.* **2017**, 56, 7653.
- [28] (a) R. Bauernschmitt, R. Ahlrichs, *Chem. Phys. Lett.* **1996**, 256, 454. (b) R. E. Stratmann, G. E. Scuseria, M. J. Frisch, *J. Chem. Phys.* **1998**, 109, 8218. (c) M. E. Casida, C. Jamorski, K. C. Casida, and D. R. Salahub, *J. Chem. Phys.* **1998**, 108, 4439.
- [29] For a recent review, see: S. Mirabella, F. Cardona, A. Goti, *Org. Biomol. Chem.* **2016**, 14, 5186.
- [30] (a) J. Du Bois, C. S. Tomooka, J. Hong, E. M. Carreira, *J. Am. Chem. Soc.* **1997**, 119, 3179. (b) K. Guthikonda, P. M. Wehn, B. J. Caliendo, J. Du Bois *Tetrahedron* **2006**, 62, 11331.
- [31] The 1,2-*cis* configuration was explained by the bulkiness of the O4 and O6 protecting group, see: A. Imamura, N. Matsuzawa, S. Sakai, T. Udagawa, S. Nakashima, H. Ando, H. Ishida, M. Kiso, *J. Org. Chem.* **2016**, 81, 9086.
- [32] Pre-addition of an excess amount of alcohols gave the 1,2-aminoalcoxyated product in good yield, see: T. Murakami, Y. Sato, K. Yoshioka, M. Tanaka *RSC Adv.* **2014**, 4, 21584.
- [33] A. Walczewska, D. Grzywacz, D. Bednarczyk, M. Dawgul, A. Nowacki, W. Kamysz, B. Liberek, H. Myszk, *Beilstein J. Org. Chem.* **2015**, 11, 869.
- [34] (a) J. A. Souto, P. Becker, Á. Iglesias, K. Muñiz *J. Am. Chem. Soc.* **2012**, 134, 15505. (b) J. A. Souto, C. Martínez, I. Velilla, K. Muñiz, *Angew. Chem. Int. Ed.* **2013**, 52, 1324. (c) L. Fra, A. Millán, J. A. Souto, K. Muñiz, *Angew. Chem. Int. Ed.* **2014**, 53, 7349. For a recent review on amination with hypervalent iodine, see: (d) K. Muñiz, *Top. Curr. Chem.* **2015**, 373, 105.

COMMUNICATION



N-acyliminoiodinanes have been characterized for the first time by X-ray structural analysis. The *ortho*-methoxymethyl group and the carbonyl oxygen coordinate to the iodine atom of the iminoiodinane. The activation of the *N*-acyliminoiodinane was achieved by photo-irradiation at 370 nm to enable reaction with various silyl enol ethers to give α -aminoketone derivatives in good to high yield. It was also demonstrated that *N*-sulfonyliminoiodinanes bearing *ortho*-substituents could be used in the photo-induced amination.

Keywords: amination • hypervalent iodine • photoreaction

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**Ortho-effect enabled characterization
of *N*-acyliminoiodinane and its
application to photo-induced
amination**